

PROTOTYPE DEVELOPMENT AND TEST RESULTS OF A
CONTINUOUS AMBIENT AIR MONITORING SYSTEM FOR
HYDRAZINE AT THE 10 ppb LEVEL *

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ABSTRACT

A Hydrazine Vapor Area Monitor (HVAM) system is currently being field tested as a detector for the presence of hydrazine in ambient air. The MDA/Polymetron Hydrazine Analyzer has been incorporated within the HVAM system as the core detector. This analyzer is a three-electrode liquid analyzer typically used in boiler feed water applications. The HVAM system incorporates a dual-phase sample collection/transport method which simultaneously pulls ambient air samples containing hydrazine and a very dilute sulfuric acid solution (0.0001 M) down a length of 1/4 inch outside diameter (OD) tubing from a remote site to the analyzer. The hydrazine-laden dilute acid stream is separated from the air and the pH is adjusted by addition of a dilute caustic solution to a pH greater than 10.2 prior to analysis.

Both the dilute acid and caustic used by the HVAM are continuously generated during system operation on an "as needed" basis by mixing a metered amount of concentrated acid/base with dilution water. All of the waste water generated by the analyzer is purified for reuse by Barnstead ion-exchange cartridges so that the entire system minimizes the generation of waste materials. The pumping of all liquid streams and mixing of the caustic solution and dilution water with the incoming sample are done by a single pump motor fitted with the appropriate mix of peristaltic pump heads. The signal to noise (S/N) ratio of the analyzer has been enhanced by adding a stirrer in the MDA liquid cell to provide mixing normally generated by the high liquid flow rate designed by the manufacturer. An onboard microprocessor continuously monitors liquid levels, sample vacuum, and liquid leak sensors, as well as handles communications and other system functions (such as shut down should system malfunctions or errors occur). The overall system response of the HVAM can be automatically checked at regular intervals by measuring the analyzer response to a metered amount of calibration standard injected into the dilute acid stream.

The HVAM system provides two measurement ranges [threshold limit value (TLV): 10 to 1000 parts per billion (ppb)/LEAK: 100 ppb to 10 parts per million (ppm)]. The LEAK range is created by dilution of the sulfuric acid/hydrazine liquid sample with pure water. This dual range capability permits the analyzer to quantify ambient air samples whose hydrazine concentrations range from 10 ppb to as high as 10 ppm. The laboratory and field prototypes have demonstrated total system response times on the order of 10 to 12 minutes for samples ranging from 10 to 900 ppb in the TLV mode and <2 minutes for samples ranging from 100 to 1300 ppb in the LEAK mode.

Service intervals of over 3 months have been demonstrated for continuous 24 hour/day, 7 day/week usage. The HVAM is made up of a purged cabinet that contains power supplies, RS422 signal transmission capabilities, a UPS, an on-site warning system, and a Line Replaceable Unit (LRU). The LRU includes all of the liquid flow system, the analyzer, the control/data system microprocessor and assorted flow and liquid-level sensors. The LRU is mounted on a track slide system so it can be serviced in place or totally removed and quickly exchanged with another calibrated unit, thus minimizing analyzer downtime. Once an LRU is removed from an analyzer enclosure, it can be brought to a laboratory facility for complete calibration and periodic maintenance.

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INTRODUCTION

The National Aeronautics and Space Administration (NASA) and the United States Air Force (USAF) utilize hydrazine, a hypergolic propellant, as rocket fuel. The current TLV for hydrazine is 100 ppb, as established by the American Conference of Governmental Industrial Hygienists (ACGIH). A Notice of Intended Change has been issued by ACGIH to lower the limit to 10 ppb. Several facilities located at the NASA Kennedy Space Center (KSC) and Cape Canaveral Air Force Station (CCAFS) periodically load propulsion modules with hydrazine fuel. During the loading process, all personnel present in a facility wear protective clothing [self-contained atmospheric protective ensemble (SCAPE) suits] and the emphasis is on rapid response by an area monitor to leak levels (1 ppm or higher). The higher levels of hydrazine are indicative of leaks in the fueling operation and are potentially destructive to flight hardware. The NASA Instrumentation Section, Toxic Vapor Detection Laboratory (TVDL) has been tasked to develop an area monitor, which has the capability to continuously monitor and detect hydrazine vapor concentrations in the workplace which might be present at both the proposed 10 ppb TLV level, as well as at leak levels as high as 10 ppm. This report presents the results on the development and testing of a prototype area monitor analyzer system capable of meeting these requirements and operating unattended for 90 days (24 hour/day) on a continuous basis.

HARDWARE

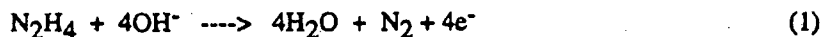
The HVAM analyzer system is contained within a purged Hoffman enclosure and is composed of two distinct sections: LRU section and an electronics section.

LINE REPLACEABLE UNIT (LRU)

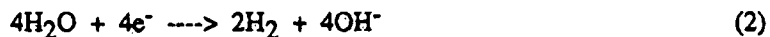
The LRU includes the hydrazine analyzer, liquid/air handling system, diagnostic sensors, and the control/data system microprocessor. The LRU is mounted on a retractable track slide system so that it can be easily serviced in place or totally removed and quickly exchanged with another calibrated unit, thus minimizing analyzer downtime.

Hydrazine analyzer

The MDA/Polymetron hydrazine analyzer, manufactured by the MDA Company, is used as the sensing portion of the HVAM system. The MDA is a rugged process analyzer designed for the continuous on-line measurement of 0 to 1000 ppb hydrazine in boiler-feed water. The analyzer utilizes an amperometric electrochemical technique to oxidize hydrazine on the surface of a platinum working electrode according to equation 1:



At the same time, reduction of water to produce hydrogen gas takes place at the cathode, or counter electrode (equation 2):



A stainless steel disk is used as the counter electrode. During the electrochemical process a current is produced whose magnitude is proportional to the concentration of hydrazine in the sample. In order to minimize the zero drift of the system due to changes in the composition of the sample water and to the electrolysis current, the MDA analyzer uses a Ag/AgCl reference electrode as part of the electrochemical setup. The microprocessor-controlled potentiostat maintains a constant potential on the platinum working electrode compared to the reference electrode.

The electrochemical reaction occurring within the cell is temperature sensitive. In order to automatically

compensate for temperature variations of the liquid sample, the measuring cell is equipped with a temperature sensor. The output from this sensor is used to reference all hydrazine concentrations to a temperature of 25 °C.

Liquid Flow System

The pumping of all liquid or air/liquid samples is accomplished using a Baldor single- phase, right-angle AC gear motor, running at 77 revolutions per minute (rpm's), equipped with two types of peristaltic pump heads: 1) Cole-Parmer L/S standard pump heads to transfer water from the waste reservoir to the Barnstead ion exchange columns for purification and to deliver clean dilution water to the pumping system; 2) Ismatec 8-station minicartridge pump head to transfer dilute acid/base solutions, or to pump the sulfuric acid/hydrazine sample from the gas/liquid separator. The tubing for either the individual Ismatec cartridges or the L/S standard pump heads is Pharmed™, manufactured by the Norton Co., and is sized to deliver liquid at a specific rate based on the RPM of the pump motor. This tubing is an EPDM rubber blend material that is very suitable for use with dilute acid/base solutions. The liquid flow system is shown in Figure 1.

A Piab eductor pump is used to draw a liquid/vapor sample down a length of 1/4 inch OD Bev-a-line IV tubing. The air flow rate in the sample tubing, nominally 5 liters per minute, is monitored by means of a 1-10 LPM rotometer whose inlet is plumbed to a trap in case any liquid sample is pulled past a gas/liquid separator. The outlet line from the Piab pump is vented through a bulkhead fitting in the wall of the Hoffman enclosure. Since the vented air stream could contain entrained acid droplets, it is not returned to any cleanroom area.

The basic impinger method of trapping a vapor sample in a scrub liquor has been modified in order to deliver a liquid sample to the MDA analyzer. The plastic sample block (Figure 2) joins the air sample, acid delivery line, and the acid/air sample return line. A steady stream of dilute sulfuric acid H_2SO_4 is continuously pumped out to the plastic sample block and dripped into the air stream. The air/dilute acid mixture is pulled down a length of 1/4 inch OD Bev-a-line IV sample line "scrubbing" the hydrazine into the dilute acid solution. The delivery end of the sample line is connected to a gas/liquid separator within the purged enclosure, which pulls the hydrazine-laden dilute acid solution away from the air. The remaining liquid sample is mixed with dilute NaOH in order to raise the solution pH to a value greater than 10.2. The amperometric measurement of hydrazine by the MDA analyzer is dependent on the sample pH being above 10.2. If the analyzer is operating in the LEAK, i.e., HIGH FLOW mode, additional water is added to the sample in order to dilute any high concentrations of hydrazine and keep the signal from the MDA onscale in its inherent 1 to 1000 ppb range. While in this mode, the output from the MDA is adjusted by the on-board microprocessor to compensate for the water dilution.

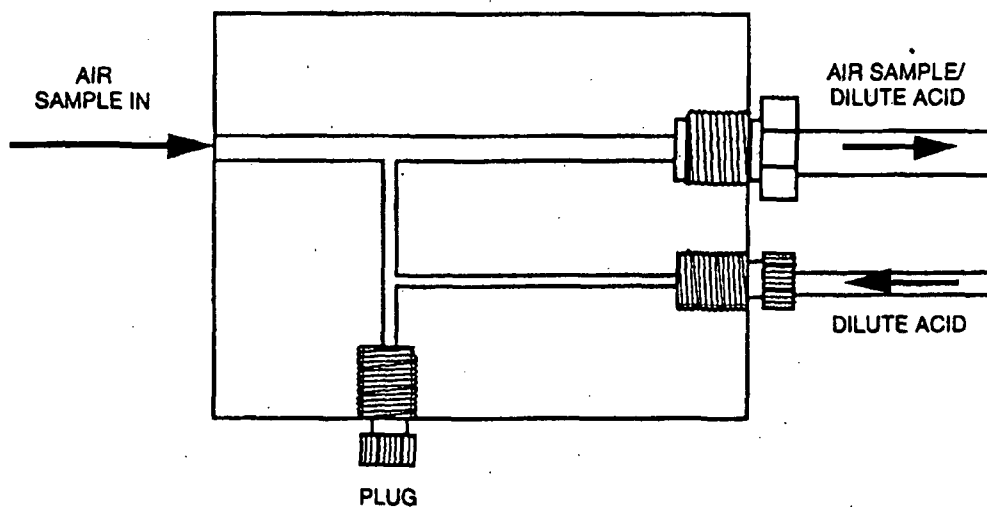


Figure 2 - Hydrazine Area Monitor Sample Block

All of the wastewater samples generated by the analyzer are cleaned of residual hydrazine, acid, and base by means of a series of Barnstead ion-exchange cartridges. The first is a high-capacity 2-bed ion-exchange cartridge. The second is a combination organic-removal, ultrapure-cartridge composed of activated carbon and a mixed-bed resin. An in-line conductivity sensor tests the output water from the first cartridge as a check of filter cartridge lifetime. A color change in the conductivity sensor light from green to red indicates that the first filter cartridge has

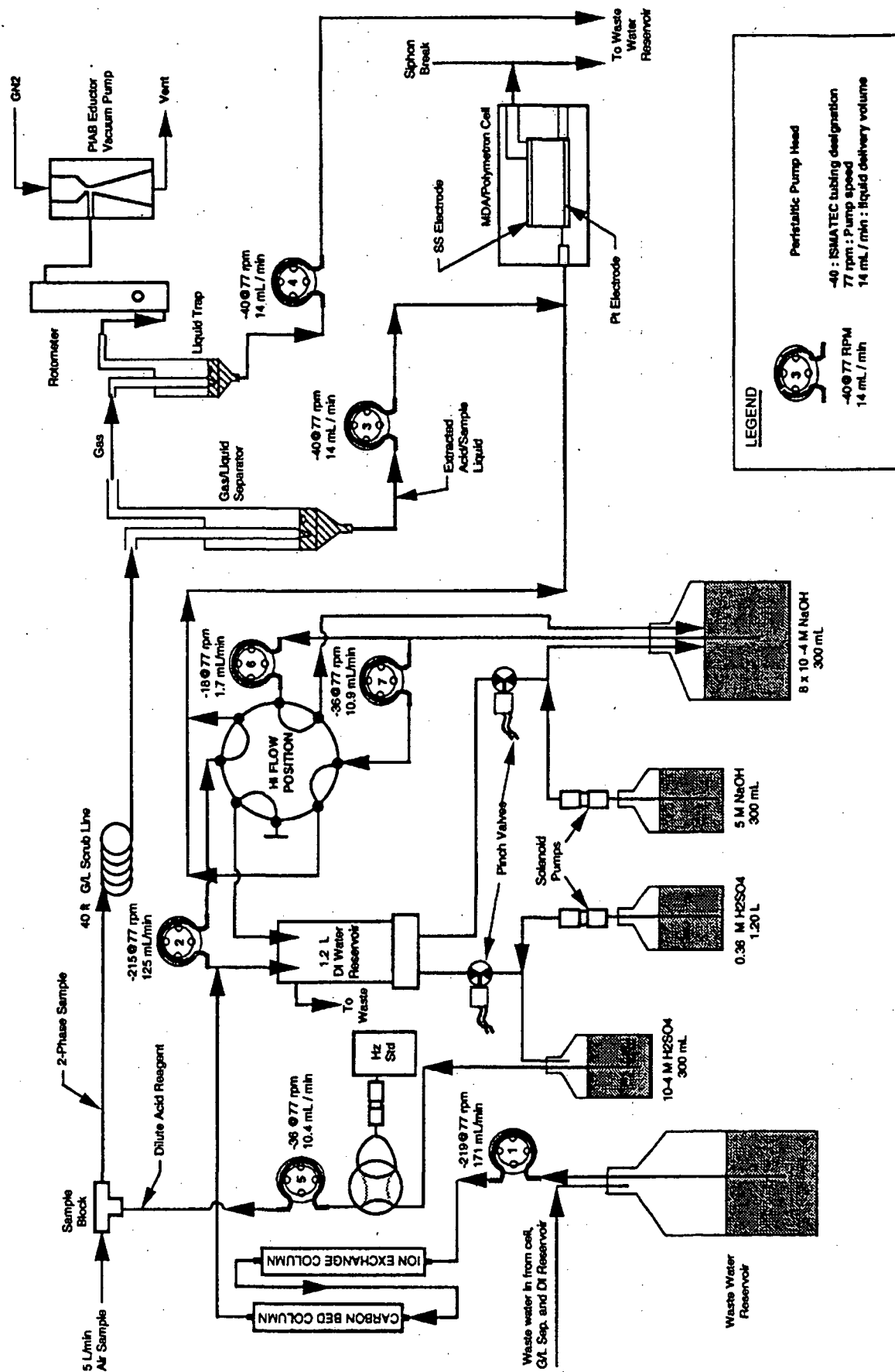


Figure 1 - Acid/Sample Extraction With Dual Range MDA/Polymetron and Water Purification Flow Scheme (High Flow Position)

failed and should be replaced. The flow rate of water out of the Barnstead cartridges is fast enough to supply adequate water to the clean water reservoir as well as the dilution water needed when the system is in the LEAK mode.

Both the dilute acid and base solutions needed during the operation of the analyzer system are generated on an "as needed" basis. Two liquid reservoirs contain the undiluted acid and base. The volumes of these containers (300 milliliter (ml) base; 1200 ml acid) have been sized such that enough liquid is present for a 3-month analysis period. Preparation of a diluted acid/base sample is accomplished by adding a metered amount of undiluted acid/base to a volume of purified water. The diluted acid solution is continuously pumped out to the sample block, while the diluted base solution is mixed with the incoming sample after the gas/liquid separator.

The preparation of fresh acid/base samples during the operation of the system is based on sensing the level of liquid present in the diluted reagent reservoirs. Each diluted reagent reservoir contains 2 LED-type liquid-level sensors. The top FULL sensor is located 1 to 2 inches from the top of the reservoir, while the bottom EMPTY sensor is positioned 1 to 2 inches from the bottom of the reservoir. The volume of liquid between the two sensors is 160 to 170 ml. A fill cycle for either dilute reagent reservoir is initiated when the output for both sensors within the reservoir indicates they are simultaneously uncovered. During the fill cycle, a metering pump delivers a preset amount of undiluted acid or base into a stream of clean water being added to the dilute reagent reservoir. Dilution water continues to be added until the output for both level sensors indicates they are simultaneously covered with liquid. The refilling of the dilute acid reagent reservoir takes place approximately once every 15 to 20 minutes. The base reagent reservoir is refilled every 1.5 hours when the analyzer is in the TLV mode of operation, and every 15 to 20 minutes in the LEAK mode.

During normal operation of the hydrazine analyzer, the system will operate in the TLV mode. The concentration of hydrazine present in the vapor surrounding any sampling point should be below both the present TLV of 100 ppb and the proposed TLV of 10 ppb. Periodically, propulsion modules within a facility will be filled with hydrazine propellant. Since leaks may occur during this filling operation, workers are required to wear protective SCAPE clothing. Typically, action must be taken if the concentration of the leak reaches 1 ppm. The analyzer must be able to track hydrazine vapor concentrations as high as 10 ppm during these periods. Since the MDA analyzer can only output concentrations between 0 and 1000 ppb, it is necessary to dilute the liquid sample delivered to the analyzer during the LEAK mode of operation. This is accomplished by means of a VALCO air-actuated 8-port rotary valve. Switching of this valve, which can be accomplished remotely over the RS232/422 communications link, from the TLV mode to the LEAK mode increases the amount of diluted base added to the incoming sample as well as adding dilution water. When the analyzer is not in LEAK mode, the extra base is returned to the base dilution vessel. The addition of water to the incoming sample allows the output of the hydrazine analyzer to remain within its normal operating range of 0 to 1000 ppb. At the time when the valve switching takes place, appropriate multiplicative factors are used to ensure that signals processed over RS232/422 data lines indicate the correct concentrations. These factors are obtained during the basic vapor calibration of the analyzer system.

A liquid calibration standard (20 ppm hydrazine in 0.0001 M H_2SO_4) can be injected into the pumping system as a way of tracking the wear on the peristaltic pump tubing over the course of the 90 day maintenance period. This calibration check, which can be done either manually or automatically on a timed basis, uses a separate metering pump to make multiple injections of the calibration standard into the dilute acid stream. This acid/standard mix is pumped out to the sample point and then pulled back to the analyzer by the Piab pump described previously. The microprocessor compares the integrated MDA output for the injected amount of standard to the initial calibration integral taken during the analyzer maintenance cycle. The ratio of the two integrals is used in adjusting the hydrazine concentration output by the microprocessor. A historical log of all the calibration checks initiated during a 90-day maintenance period is kept by the microprocessor.

Diagnostic Sensors

The analyzer system has been equipped with several diagnostic sensors which are continuously checked by the onboard microprocessor:

- Acid/Base Reservoir Sensors: Liquid-level sensors (LED type) are present in both the concentrated acid and base reservoirs. An operator is alerted every 30 minutes if the level of liquid in either of these containers is low.
- Leak Sensor: Leaks which occur in the pumping system during analyzer operation, drip onto the waste

water reservoir cover, filling an indentation located in one corner of the reservoir top. A liquid-level sensor (LED type) is positioned inside of this indentation and is activated once the level of liquid reaches the sensor tip. Once a leak has been sensed, the pumping system will be shut down by the microprocessor and an appropriate error message sent to the operator.

- **RPM Sensor:** This sensor is positioned over the rotating shaft of the Baldor motor. The on-board microprocessor updates the RPM value every minute and shuts off the pumping system if the observed value is out of tolerance.

- **Vacuum Switches:** Two vacuum switches have been placed upstream from the rotometer and Piab pump assembly. The first, or HIGH VACUUM switch, is used to check for a blocked vapor sample line. In comparison, the LOW VACUUM switch is used to check for the presence of an open gas line in the pumping system or vacuum source failure. If an error condition is indicated on either of these switches, the microprocessor will shut down the entire pumping system. This prevents possible spillage of the dilute acid at the sampling block in the event of line blockage or loss of vacuum.

Control/Data System Microprocessor

The onboard microprocessor is a PEP VSBC-3 (68000 CPU) single board computer programmed in the C language. Inclusion of input/output piggyback modules allows the microprocessor to interrogate system sensors as well as send signals to actuate solenoid valves. The hardware has also been configured to allow either RS232 or RS422 communications with external data control systems.

ELECTRONICS

The electronics section of the analyzer system can be found in the upper portion of the purged enclosure. Fixed power supplies, signal distribution, and an UPS are all mounted on a pull-out drawer for easy access. Interconnect cabling to both the LRU and terminal connectors to the enclosure is routed behind the electronics and LRU sections and held against the back wall of the enclosure by the LRU when both sections are fully retracted. The UPS is connected to the onboard microprocessor and shut off by the computer when fatal system errors are detected after proper transmission of the failure mode has been made across the RS232/422 communications link.

A Differential Pressure (DP) switch, mounted on the electronics drawer, senses the cabinet purge pressure. Should the cabinet purge be lost in any way, the DP switch signals the computer and the microprocessor shuts down the entire system. Also, if the AC power to the box is lost or interrupted, the computer will initiate a shutdown of all processing functions as well as turn off the power to the UPS.

RESULTS

HYDRAZINE STANDARDS GENERATOR

All of the hydrazine vapor standards used during the test program were generated under controlled conditions of temperature (25 °C) and relative humidity [45 percent relative humidity (RH)]. The Kin Tek Span Pac (Model 361), a precision standard toxic vapor generator, was used to produce controlled concentrations of hydrazine vapor for further dilution.

The Miller Nelson Model HCS-301, a completely automated system, was used to precisely control the flow, temperature, and RH (F/T/RH) of the diluent air to provide the desired hydrazine vapor concentrations. Two F/T/RH controllers were used during analyzer testing, one for providing diluent to the hydrazine sample vessel and the second for providing a hydrazine-free "zero" sample. The hydrazine vapor produced by the standards generator was mixed with the diluent air from the F/T/RH controller at a Teflon injection tee upstream of the hydrazine sample vessel. The sample vessels containing hydrazine and "zero" air were connected by means of a 3-way GALTEK solenoid valve. The position of this valve was controlled by a data acquisition system (DAS) to deliver the appropriate sample for analysis. The concentrations for all of the standards used during the testing were confirmed by impingement coulometric titration.

LINEARITY

During laboratory testing of the HVAM, the response of the system was monitored and compared to the input value for known hydrazine vapor standards (Figure 3). The dashed lines represent the ± 5 percent error around the ideal response (HVAM Output = Hydrazine Vapor Input) published by MDA for the core sensor of the HVAM. The overall response of the system, represented by the square symbols, is quite linear up to approximately 1000 ppb. The solid line is the best first order fit ($r^2 = 0.992$) of the experimental data for the HVAM in the TLV mode, and it falls within the quoted error of the MDA cell through the entire measured range.

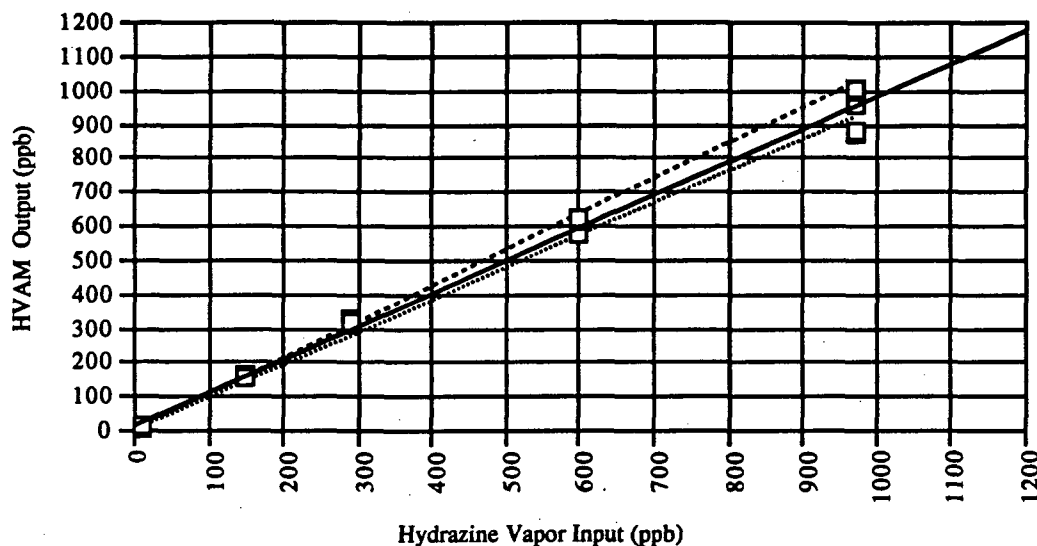


Figure 3 - Hydrazine Area Monitor Linearity (Low Flow/TLV Mode)

In the LEAK mode of operation, the HVAM system is designed to add clean water to the incoming sample in order to keep the output of the MDA core sensor onscale in its inherent 0 to 1000 ppb range. While operating in this mode, the onboard VME microprocessor multiplies the MDA response by a vapor calibration ratio in order to properly reflect the dilution of the incoming sample. The calibration ratio shown in equation 3 is based on the observed MDA responses to a calibration span standard when measured in both TLV and LEAK flow during the initial vapor calibration of the analyzer.

$$\text{Vapor Calibration Ratio} = (\text{MDA Cal Response})_{\text{TLV}} / (\text{MDA Cal Response})_{\text{LEAK}} \quad (3)$$

The data shown in Figure 4 were obtained by processing a series of hydrazine vapor samples while the analyzer system was operating in the HI FLOW (LEAK) mode. The HVAM output values have been adjusted by the microprocessor to reflect the dilution of the incoming sample. As in Figure 3, the dashed lines above and below the best straight line fit represent the ± 5 percent error standards published by MDA. The overall response of the system, represented by the square symbols, is again quite linear. The solid line is the best first order fit ($r^2 = 0.99$) of the experimental data for the HVAM in the LEAK mode, and it falls on top of the -5 percent error of the MDA cell through the entire range.

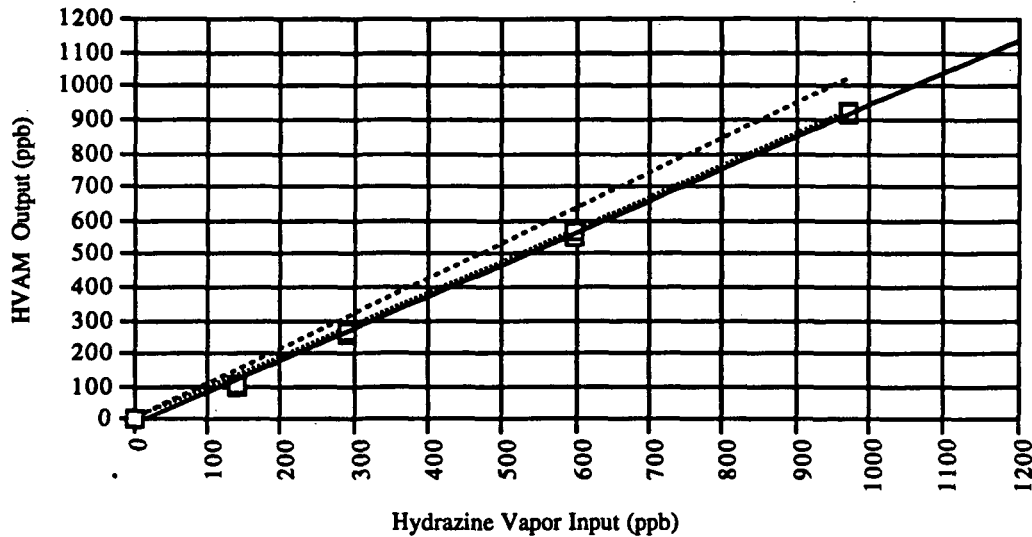


Figure 4 - Hydrazine Area Monitor Linearity (Hi Flow/Leak Mode)

REPEATABILITY

The ability of the HVAM to consistently quantify standard vapor samples was tested for an extended period of time prior to deployment in the field. The concentrations of the vapor samples ranged from 10 to 1000 ppb and were generated by the hydrazine vapor generator system mentioned in a previous section. The output of the HVAM for a nominal 10 ppb vapor sample is shown in Figure 5. The response of the analyzer to this concentration is of particular interest since it has been proposed that the current TLV level of 100 ppb be lowered to 10 ppb. During those periods of time for which there is no HVAM output, the analyzer system was sampling room air.

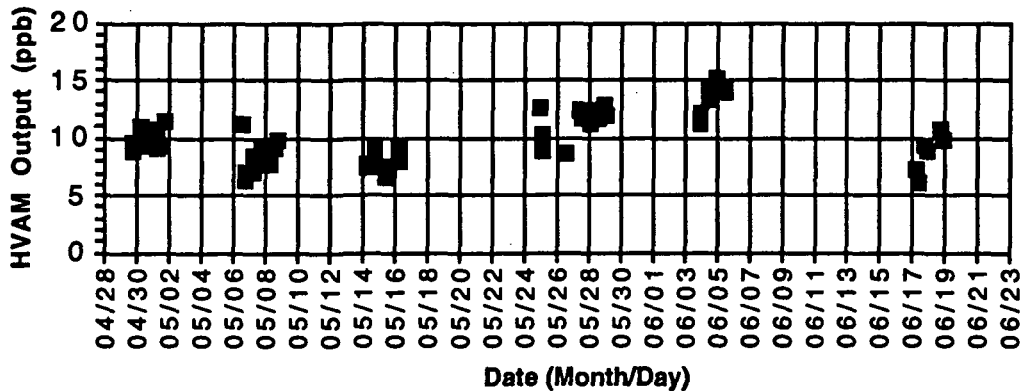


Figure 5 - HVAM Repeatability Data at the 10 ppb Level

LIQUID CALIBRATION CHECKS

The Pharmed™ pump tubing used in the peristaltic pumping system of the HVAM may change its delivery rate during the 90 day maintenance cycle of the analyzer. In order to compensate for any changes in the pumping system, checks can be done using an onboard calibration sample. A liquid calibration cycle, which can be initiated either manually from an operator console or automatically on a software-controlled timed basis, injects a known amount of a dilute acid-hydrazine standard (20 ppm hydrazine in 0.0001 M sulfuric acid) into the acid stream which is pumped out to the sample block. The microprocessor collects a time-based integral of the MDA output from the calibration sample and compares it to the value for the same injection sample taken during laboratory calibration. A ratio of these two integrals can be expressed by equation 4:

$$\text{Liquid Calibration Ratio} = \text{Current Integral/Initial Integral} \quad (4)$$

where: Current Integral is the latest value for the calibration injection sample.
Initial Integral is the value for the calibration injection sample taken during laboratory calibration.

A separate liquid calibration ratio is obtained for both TLV and LEAK modes of operation. Prior to output over RS422/232 data lines, the MDA response is adjusted for both the flow characteristics of the system (TLV/LEAK) and the current value of the liquid calibration ratio. Equation 5 shows how both of these factors are used in arriving at the final system response.

$$\text{HVAM Response} = \frac{\text{MDA Response} * \text{Vapor Calibration Ratio(TLV/LEAK)}}{\text{Liquid Calibration Ratio(TLV/LEAK)}} \quad (5)$$

In TLV mode, the Vapor Calibration Ratio is set equal to one, since no compensation needs to be made for dilution water. The data presented in Figure 6 represent the values for the liquid calibration ratios taken in TLV mode during a 2-month period of analyzer operation. The data taken for standard vapor samples ranging from 10 to 1000 ppb hydrazine remained essentially constant throughout the 2-month sampling period despite the observed changes in the liquid calibration checks. The two spikes in the liquid calibration data are indicative that a dramatic change took place in the pumping system for two short periods of time, but the analyzer was able to recover and perform satisfactorily.

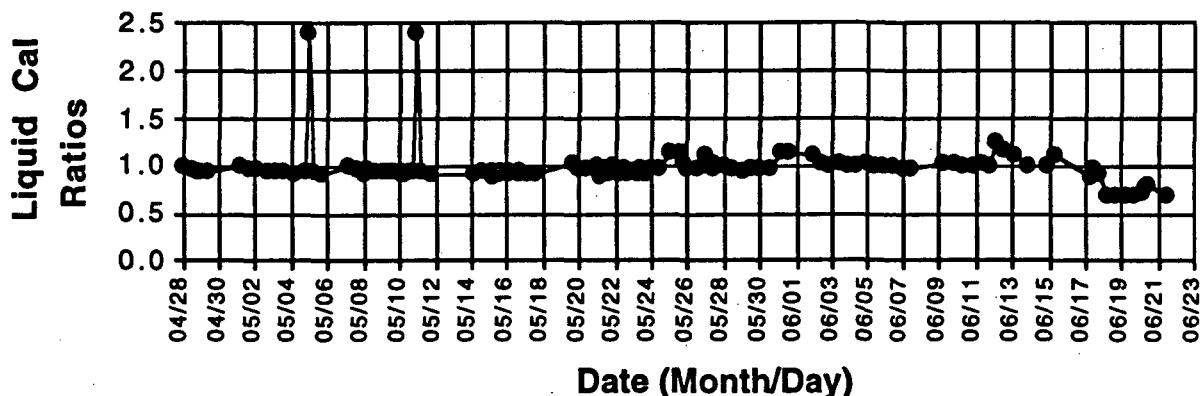


Figure 6 - Liquid Calibration Checks (TLV Mode)

CONCLUSIONS

The HVAM is a complete system capable of detecting hydrazine vapors in ambient air at concentrations from 10 ppb to greater than 1 ppm. In order to provide this dynamic range, the HVAM can be manually switched to cycle between TLV and LEAK modes, depending on the operation to be monitored. The system can operate maintenance-free without either reagent or water makeup for 90 days and is designed with a number of safeguards to automatically shut down in case of a power failure, an internal liquid leak, a pump failure, or loss of purge within the enclosure. The LRU has been designed to simplify maintenance and allow for a quick changeout of the core analyzer system to minimize analyzer downtime.

Test results to date indicate a stable baseline, with only a 2 to 3 ppb drift over two months of operation. The output of the HVAM for a nominal 10 ppb input vapor sample was stable, with a random scatter of about +/- 4 ppb. Performance checks using liquid calibration standards indicated that the pumping and tubing system was also stable during this period.

ACKNOWLEDGMENTS

The authors wish to thank all the members of the HVAM team for their work on the analyzer system. The HVAM team includes personnel from the TVD/Contamination Monitoring (CM) Laboratory, McDonnell Douglas Space Systems, I-NET Space Services, and NASA.